

1922

F24

CALCIUM CARBIDE AS AN AGENT FOR
REMOVING PHOSPHOROUS AND
SULPHUR FROM IRON AND
STEEL

BY

WILLIAM JAMES FARRELL, Jr.

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1922



Digitized by the Internet Archive
in 2015

<https://archive.org/details/calciumcarbideas00farr>

1522
F 24

UNIVERSITY OF ILLINOIS

May 25 1922

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

William James Farrell, Jr.

ENTITLED Calcium Carbide as an Agent for Removing Phosphorous
and Sulphur from Iron and Steel

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

W. S. Putnam

Instructor in Charge

APPROVED:

ACTING HEAD OF DEPARTMENT OF CHEMISTRY

CONTENTS

	Page
Acknowledgement	
Introduction	1
Discussion	2
Laboratory Work	9
Methods of Analysis	9
Experimental Work	15
Results of Analysis	27
Summary of Results	28
General Summary	29
Conclusions	30
Suggestions For Further Work	30
Bibliography	31

ACKNOWLEDGEMENT

I wish to express my sincere thanks to Dr. W. S. Putnam for the keen interest he has shown towards this work, and for the untiring efforts and many helpful suggestions he has made.



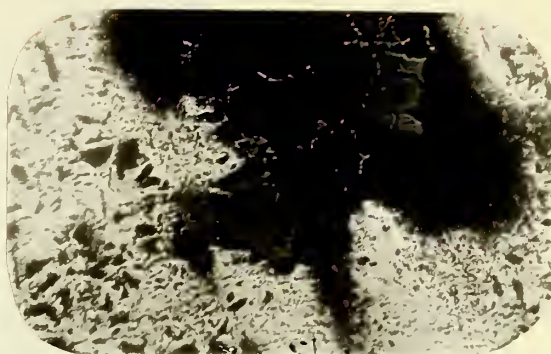
INTRODUCTION

Sulphur and phosphorous are the most harmful and most common enemies of steel. It is true that oxygen and nitrogen produce detrimental effects, but with proper treatment this objection can be overcome. Sulphur occurs as ferrous sulphide or as manganese sulphide and phosphorous exists as phosphides of iron. Sulphur is equally as harmful in cast iron as it is in steel, however, small amounts of phosphorous, not exceeding 0.10%, are permissible in cast iron. Up to the present time, no commercial process has yet been devised whereby these elements have been entirely removed. They have, however, been reduced to a point as low as 0.01 per cent, but even this small amount produces detrimental effects, due to segregation in certain parts of the ingot, which not only cause trouble during forging in the case of steel, but also produce red shortness and coarse grained structure during casting.

The patch of metal in which these segregations occur possesses all the properties of very inferior steel or iron, although the average composition of the remainder of the metal is excellent and an analysis of the drillings failed to reveal this trouble.

One of the best methods for detecting a sulphur segregation is to obtain a representative polished surface and then press a piece of photographic paper, previously soaked in hydrochloric acid, against this surface. If a sulphur segregation is present fumes of hydrogen sulphide will be generated which will produce a brown stain upon the paper.

These segregations can also be detected by taking a microphotograph of a polished surface. An analysis of the drillings may fail to reveal sulphur segregations, but the microphotograph will have an appearance similar to that shown in the accompanying illustration.

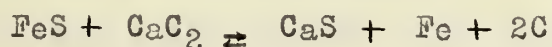


Microphotograph Showing
Sulphide Segregation.

DISCUSSION

The object of this thesis work is to devise a method whereby the elements sulphur and phosphorous can be entirely removed from steel and cast iron by use of calcium carbide as the removing agent. The work on cast iron was not taken up until after several tests had been made on low carbon steel, and it was found that temperatures required to produce the desired fluidity of the molten metal could not be obtained with the types of furnaces at hand. An electric furnace capable of producing temperatures as high as 2000 degrees C. was being constructed, by Mr. J. E. Fritts, but due to delay in delivery of material, was not completed soon enough to be used for this work.

The reactions by which the complete removal of sulphur and phosphorous was expected were:



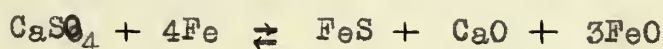
Part of the calcium carbide would probably be oxidized to calcium oxide which would produce the following reaction:



The phosphorous was to be removed by the reaction:



The chief difficulty encountered, however, is that of overcoming the great affinity iron has for these two elements, namely, phosphorous and sulphur. Iron combines so readily with sulphur and phosphorous that it is capable of uniting with these elements, when brought into contact with what are considered otherwise stable compounds. *It has been shown that iron will decompose calcium sulphate according to the reaction:



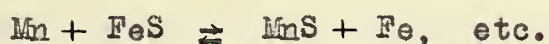
Furthermore, nearly all fuels used in the metallurgy of iron and steel contain variable amounts of sulphur, which is liberated as a gas and absorbed either directly or indirectly by the ferrous metal.

Manganese is capable of taking up sulphur from iron sulphide, but this compound, manganese sulphide, is soluble in both the basic slag and the metal, and segregations of manganese sulphide are just as detrimental to the metal as those of iron sulphide.

Because of the solubility of manganese sulphide in a basic slag, this compound rises to the surface where it can be oxidized by the oxygen of the air with which it comes in contact, and is converted into free manganese and sulphur dioxide. The sulphur dioxide passes off with the other gases, and the manganese combines

*The Basic Open Hearth Process--Dichmann--1911 p. 167

with more of the sulphur contained in the slag or metal according to the following reactions:



However, this reaction can never be carried to a point of less than 0.01 per cent sulphur due to the reversibility of the reaction as the sulphur content approaches this point.

Various other means of removing sulphur have been devised.

*Saniter has proposed the use of calcium chloride in conjunction with a basic slag rich in calcium oxide, and made fluid by the addition of calcium fluoride, but owing to the large expense in both time and money this method has never been of commercial importance.

Sulphur can be completely removed from iron only when converted into a form which is insoluble in the metal but very soluble in the slag. Calcium sulphide fulfills these conditions, but according to *1Prof. Osann, this compound can be produced only when the slag is free from metallic oxides. Otherwise, the calcium sulphide will be decomposed and metallic sulphides formed according to the following reaction:



The sulphur in the form of iron sulphide will then be

*The Basic Open Hearth Process--Dichmann--1911 p.170

*1 Stahl und Eisen--1908 pp 873 and 1071

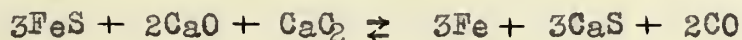
immediately returned to the metal.

In order to keep the slag free from metallic oxides, reducing agents such as calcium carbide must be present and for possibility of the carbide free from metallic oxides very high temperatures are required. It is because of the necessity of these very high temperatures that the Basic Open Hearth process fails to produce steel absolutely free from sulphur segregations.

*Dr. Richard Moldenke has stated that a new desulphurizing agent (probably a potassium compound) had attained a wide vogue in Germany. This compound, when added to the molten metal, contained in a ladle, produces a vigorous reaction, and a thin slag forms, which can be skimmed off after absorption by a small amount of calcium oxide. A reduction to 0.03% sulphur occurred.

During recent years, experience with the production of steel in electric furnaces has apparently furnished full explanation of the conditions necessary for the complete removal of sulphur and phosphorous from steel.

*1 Sulphur may be removed in electric furnaces by use of calcium carbide, after complete deoxidation of the metal and slag according to the following reactions, forming calcium sulphide, which passes into the slag:

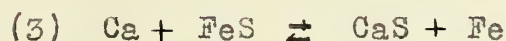


Very high temperatures are required for this reaction and the arc furnace is best adapted to produce the required temperature.

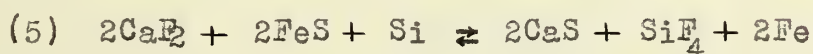
*Chem & Met--May 10, 1922 p. 887

*1 The Making, Shaping and Treating of Steel Camp and Frances
1920 p. 286

*Sulphur can be removed by use of silicon according to the following reactions: (1) $\text{FeS} + \text{Si} \rightleftharpoons \text{Fe} + \text{SiS}$



The silicon sulphide formed partly escapes as a gas. If calcium fluoride is used in place of calcium oxide for the reaction (2), then the reactions,



would occur, and the resulting calcium sulphide would pass into the deoxidized basic slag.

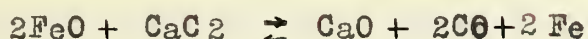
*1 According to F. T. Sisco, the desire to remove phosphorous and sulphur in electric furnace processes, often results in the production of ingots full of blow holes. This he says, is due to the fact that carbide slags saturated with calcium sulphide lose their efficiency as a deoxidizing agent, and high carbide slags become saturated when they contain 3.5 per cent of calcium sulphide. Further additions of calcium carbide to the slag as desulphurizing and dephosphorizing continues will result in the production of metal containing only traces of these elements. However, it must be remembered that deoxidation is also desired, and therefore, during the deoxidizing period the slag must be kept in a reducing condition with only a low content of calcium sulphide. If these

*Electric Furnaces in the Iron and Steel Industry--

Rodenhauser, Schoenawa, Vom Baur--1917 380-382

*1 Chem & Met.--Jan. 4, 1922 pp 17-23

conditions exist then the calcium carbide will deoxidize the molten metal according to the reaction:

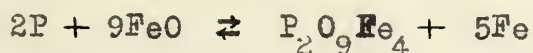


The electric furnace is now thoroughly established and the fact that no impurities are introduced during operation, along with the fact that very high temperatures and complete refining conditions exist, make it the ideal type of furnace used for the manufacture of steel.

PHOSPHOROUS

This element, although not as objectionable as sulphur should never be present in steel in amounts greater than 0.10 per cent, as it tends to produce a coarse grained structure and segregate in spots.

*As to the removal of sulphur, it requires 1.29 per cent of oxygen for each per cent of phosphorous present in order to convert it into a form insoluble in the metal but soluble in the basic slag. Oxidation can be derived only from metallic oxides and not from lime as was previously supposed. Phosphorous can be converted into an insoluble form by the following oxidation reaction:



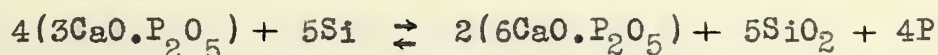
In this form phosphorous can be removed from the steel, but this compound is easily attacked by reducing agents and will exist only in oxygenous surroundings.

*1 According to Stoughton, this insoluble phosphorous compound exists as $3\text{CaO} \cdot \text{P}_2\text{O}_5$ and unless the recarburizer is added to

*Basic Open Hearth Process- Dichmann 1911 p.158

*1 The Metallurgy of Iron and Steel- Stoughton 1913 p. 136

the metal after it has been separated from the slag the following reactions will take place causing the decomposition of this phosphorous compound and the return of phosphorous to the metal:



Therefore, in practice the recarburizer is usually added to the metal, as it is pouring from the furnace.

*Georges Vié states that the relative oxidizability of phosphorous when present in molten iron is lower the higher the temperature and that above 1400 degrees C. it is less oxidizable than manganese, silicon or carbon.

*L'Age de fer, 36, 189-191

LABORATORY WORK

Various samples of iron and steel were treated with calcium carbide. Some of these samples before treatment with calcium carbide were treated with iron sulphide and ferrous phosphate to increase the sulphur and phosphorous content.

The following system of marking the specimens was used. Five tests were made and these tests were numbered from one to five. The original specimen was marked with the number corresponding to the test. Then the specimen which was treated to increase the sulphur and phosphorous content was marked with the number of the corresponding test and the letter "A" beside it. After this high sulphur and phosphorous content sample had been treated with calcium carbide it was marked with the corresponding number of the test and the letter "B" beside it.

*Methods of Analysis

Each sample was analyzed before and after each treatment to determine the carbon, phosphorous and sulphur content.

Determination of Total Carbon

Total carbon was determined by direct combustion with oxygen. The combustion train as shown in Fig. 4, was used. The sample of iron or steel was placed in an alundum combustion boat, and this combustion boat was placed in the center of a quartz tube, which was heated to a temperature of 1,000 degrees C by means of an electric resistance furnace. The pressure exerted by the water con-

*The Examination of Iron, Steel and Brass--Hall and Williams

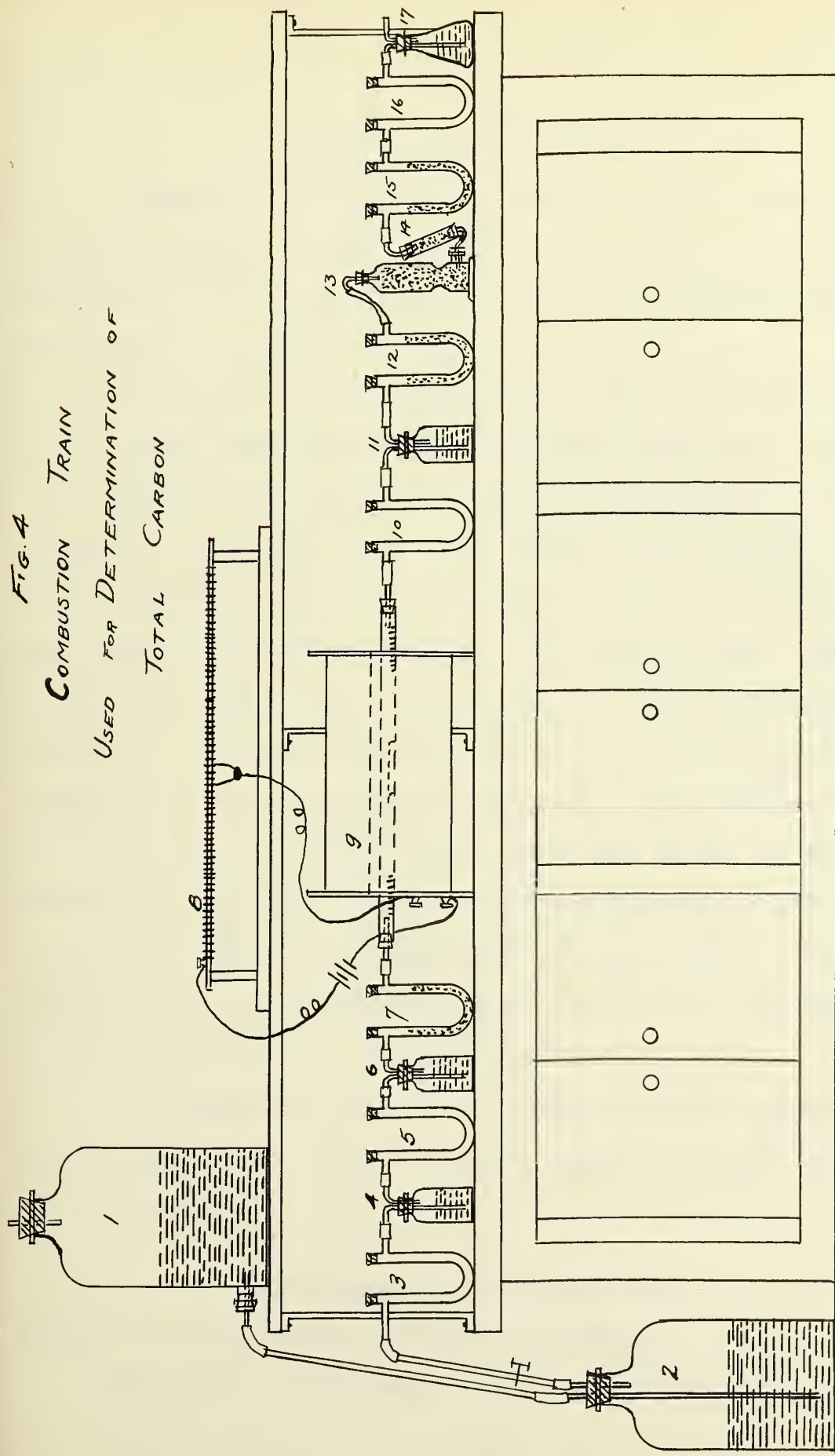


tained in the upper eight liter aspirator bottle forced the oxygen out of the lower aspirator bottle and thru the combustion train. Before coming into contact with the sample the oxygen passed thru a concentrated sodium hydroxide solution followed by concentrated sulphuric acid.

The oxygen then passed over a coil of copper oxide and came into contact with the sample of steel, oxidizing any carbon present to carbon dioxide. The resulting gases passed over another copper oxide coil, then thru a concentrated solution of chromic acid, which removed any oxides of sulphur present, and into the *absorption tower. Here the carbon dioxide reacted with the sodium hydroxide (commercial lye), contained in this tower, forming sodium carbonate and water. The water was absorbed by phosphorous pentoxide contained in the attached tube, and the excess oxygen passed on thru the barium hydroxide solution, causing the precipitation of barium carbonate if any carbon dioxide remained in the gas.

The absorption tower was weighed before and after absorption of carbon dioxide, and the difference in weight gave the weight of carbon dioxide formed during combustion. From this weight and by knowing the weight of steel used, the percentage of carbon present in the original sample was calculated.

FIG. 4
COMBUSTION TRAIN
USED FOR DETERMINATION OF
TOTAL CARBON



- | | | | |
|---------------------------|----------------------|----------------------------|--------------------------|
| 1 & 2 - Aspirator Bottles | 6 - Conc. H_2SO_4 | 10 - Chromic Acid Trap | 14 - P_2O_5 Tube |
| 3 - NaOH Trap | 7 - $CaCl_2$ | 11 - Chromic Acid Solution | 15 - $CaCl_2$ |
| 4 - NaOH Solution | 8 - Resistance | 12 - $CaCl_2$ | 16 - $Ba(OH)_2$ Trap |
| 5 - H_2SO_4 Trap | 9 - Electric Furnace | 13 - Absorption Tower | 17 - $Ba(OH)_2$ Solution |

Determination of Sulphur

Sulphur was determined in both iron and steel by the Bamber Method, which was chosen because it is reputed to give the most accurate results, even though it requires slightly more time than the various volumetric methods.

Procedure: Five grams of the sample was dissolved in conc. nitric acid, and after being completely dissolved, two grams of solid potassium nitrate was added and the solution evaporated to dryness on the water bath. The residue was heated to redness, and after cooling, 50 cc of a one per cent sodium carbonate solution was added and heated to boiling. The solution was filtered and the precipitate washed thoroughly with a one per cent sodium carbonate solution. The resulting filtrate was acidified with dilute hydrochloric acid and evaporated to dryness. The residue was moistened with 2 cc. of conc. hydrochloric acid and 50 cc. of distilled water added, and filtered. The filtrate was diluted to 100 cc. and 30 cc of a two per cent barium chloride solution added. The resulting precipitate, barium sulphate, was separated by filtration, dried, ignited and weighed in the usual manner.

The resulting precipitate contains 13.85% sulphur and by knowing the weight of the original sample the per cent of sulphur was calculated.

Determination of Phosphorous

Preparation of Ammonium Molybdate Solution:

Solution 1. One hundred grams of 85% molybdic acid was placed

in a beaker and 240 cc of water and 140 cc of ammonium hydroxide solution, d. 0.90, added. The solution was filtered and 60 cc of conc. nitric acid added.

Solution 2. 400 cc of conc. nitric acid and 960 cc of distilled water were mixed.

When solution 1 and 2 were cooled, solution 1 was added to solution 2 with constant stirring. Then 0.1 gr. of ammonium phosphate dissolved in 10 cc of distilled water was added with constant stirring and after standing for 24 hours the resulting solution was ready for use.

Preparation of Magnesia Mixture:

Fifty grams of anhydrous magnesium chloride were dissolved in 750 cc of distilled water and then 150 cc of ammonium hydroxide, d.o. 90, was added.

Procedure: Five grams of steel was weighed into an Erlenmeyer flask and dissolved in 75 cc of conc. nitric acid. The resulting solution was heated to boiling and 12 cc of strong potassium permanganate was added and boiling continued until manganese dioxide precipitated. The manganese dioxide precipitate was dissolved by the addition of ammonium bisulfite solution, an excess being avoided. The resulting solution was boiled until clear and free from brown fumes. The solution was cooled to 35 degrees C and 100cc of ammonium molybdate solution added. After standing for one minute the solution was shaken for three minutes and filtered. The precipitate was washed three times with a two percent nitric acid solution to free it from iron. Then it was

washed with a ten per cent solution of ammonium hydroxide and the resulting solution allowed to run into a 100cc beaker containing 10cc of conc. hydrochloric acid and 0.5 gr. of citric acid. 30cc of conc. ammonium hydroxide was added and then 10cc of the magnesia mixture added very slowly with constant stirring. After two hours the solution was filtered and washed with a ten per cent ammonium hydroxide solution. The precipitate was then placed in a porcelain crucible, ignited and weighed. The weighed precipitate, $Mg_2P_2O_7$, contains 27.84 per cent phosphorous and from this value the per cent of phosphorous in the original sample was calculated.

All the samples treated were melted in the oil pot furnace situated in the Assay Laboratory. This furnace had an outside diameter of about three feet and was about two and one half feet high. The furnace was heated by oil forced in under a gage pressure of about twenty-five pounds and mixed with a blast of air. It was possible to maintain temperatures ranging from thirteen to fifteen hundred degrees centigrade.

The molten iron or steel was poured into a sand mold made by pounding moulding sand into a crucible about twelve inches high and five inches in diameter around an iron bar which was withdrawn after the mold was finished. This mold was then dried in the electric oven at a temperature of about 130 degrees C. for several hours. An illustration of this mold is shown in Fig. 2.

In order to prevent oxidation the calcium carbide was added in covered iron crucibles. These crucibles were made of sheet iron and were about two inches in diameter at the top and about two inches high. The cover was fastened by means of a piece of iron wire. An illustration of these crucibles is shown in Fig. 3.

In test No. 4 the molten iron was poured from the crucible onto a surface of calcium carbide. The calcium carbide was sprinkled over a surface of sand contained in a roasting vessel constructed of a refractory material. An illustration of this arrangement is shown in Fig. 1.

Drillings for analysis were obtained by means of a shaper in the University of Illinois machine shop.

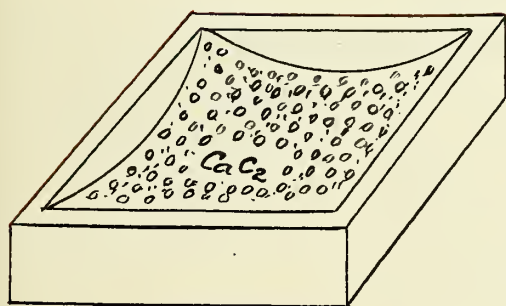


FIG. 1 - CALCIUM CARBIDE SURFACE

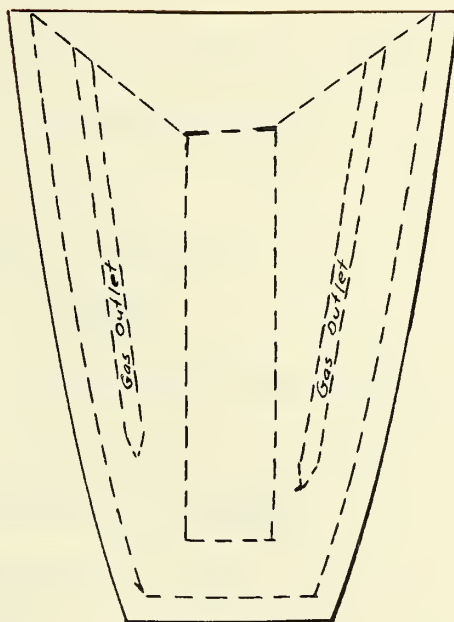


FIG. 2 - SAND MOLD.

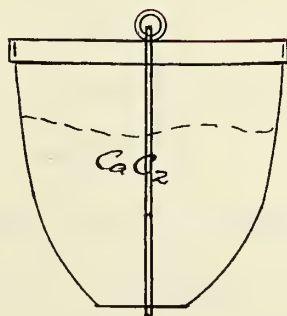


FIG. 3 - COVERED IRON CRUCIBLE
CONTAINING CALCIUM CARBIDE.

TEST NO. 1

A .38 carbon steel was used for this test and the original was marked No. 1 and gave the following analysis:

Carbon- - 0.38 %

Phosphorous- - 0.082%

Sulphur- - 0.038%

This piece was melted with the following slag in the oil pot furnace. Quantity of Steel--1,000.0 gr.

Ferrous Phosphate 26.0gr.

Calcium Fluoride 5.0

Aluminim Oxide 3.0

Ferrous Sulphide 28.0

Calcium Carbonate 10.0

Silicon di-oxide 22.0

The resulting high sulphur and phosphorous content sample was poured into the sand mold and later marked 1A. Drillings were obtained and gave the following analysis:

Carbon 0.57 %

Phosphorous 0.711

Sulphur 1.304

This high sulphur and phosphorous sample marked 1A was placed in a graphite crucible and melted with the following slag. Twenty grams of calcium carbide were added directly to the slag.

Steel 500.0 gr

Calcium Carbonate- 10.0

Calcium Fluoride 5.0

Aluminum Oxide 3.0gr.

Silicon Dioxide 22.0

Calcium Carbide 20.0

After heating in a molten condition in the oil pot furnace at a temperature of about 1500 degrees C. for one hour, the metal was poured into a sand mold and allowed to cool slowly. This sample was marked 1B and drillings were obtained and analized for carbon, phosphorous and sulphur.

The following analysis was obtained:

Carbon	3.19 %
Phosphorous	0.402
Sulphur	1.10

A comparison of the composition before and after analysis follows:

	Before Treatment	After Treatment
Carbon	0.57 %	3.19 %
Phosphorous	0.711	0.402
Sulphur	1.304	1.10
Per cent Sulphur Removed		15.69%
Per cent Phosphorous Removed		43.60%

Conclusions: This test shows that when calcium carbide is used in large amounts there is great danger of the carbon content increasing excessively, unless very high temperatures are used at which the carbide will not decompose. However, the results show a decrease in the sulphur and phosphorous content after treatment with calcium carbide.

TEST NO. 2

A sample of .38 carbon steel similar to that used in test No. 1 was used for this test, but the temperature required to produce the desired fluidity of the metal was so high that the crucible being used was melted and the charge was lost.

Due to the impossibility of obtaining temperatures high enough to produce a molten bath of the desired fluidity, the remaining tests were made on cast iron.

TEST NO. 3

The object of this test was to determine what effect additions of calcium carbide and ferrous oxide with no other slag material would produce.

A sample of cast iron, obtained at the University of Illinois foundry, was used for this test. It was analyzed for carbon, phosphorous and sulphur giving the following results:

Carbon	2.866%
Phosphorous	0.552
Sulphur	0.136

Due to the comparatively high content of sulphur and phosphorous in this original sample, no treatment to increase the sulphur and phosphorous content was required. Therefore, in the tabulated results of analysis samples No. 3 and No. 3A are both listed with the same analysis.

Eight hundred grams of this sample was placed in a crucible and heated to a molten condition in the oil pot furnace. Then fifteen grams of ferrous oxide and twenty-five grams of calcium carbide, contained in a covered iron crucible was added. Heating was continued and thirty minutes later the crucible was removed from the furnace and the molten metal was poured into a sand mold and allowed to cool slowly. This sample was marked 3B, drillings obtained and an analysis made. Results of analysis:

Carbon	1.765%
Phosphorous	0.307
Sulphur	0.129

A comparision of the analysis before and after treatment gave the following data:

	Before Treatment	After Treatment
Carbon	2.866%	1.765%
Phosphorous	0.552	0.307
Sulphur	0.136	0.129
Per cent Sulphur Removed		5.14%
Per cent Phosphorous Removed		44.38%

Conclusions: This test illustrates that phosphorous removal is at a maximum and sulphur removal at a minimum when metallic oxides are present.

The carbon content of the iron was reduced due to reaction with the ferrous oxide, but the calcium carbide was probably oxidized to lime, which caused the sulphur content to be reduced only slightly, due to the oxidizing conditions present, promoting the reaction, $\text{CaS} + \text{FeO} \rightleftharpoons \text{FeS} + \text{CaO}$.

TEST NO. 4

The object of this test was to determine what effect additions of calcium carbide at frequent intervals would produce. Furthermore, after each addition of calcium carbide, an addition of calcium carbonate was made with the object of producing an agitation of the molten metal, due to the liberation of carbon dioxide, and at the same time producing a very basic slag. This agitation was desired so that a more complete reaction between the calcium carbide and the metal would be possible.

The sample of cast iron used in this test was obtained at the University of Illinois foundry, and was marked No. 4. Drillings from this sample were obtained and an analysis made.

Results of Analysis:

Carbon	3.45 %
Phosphorous	0.440
Sulphur	0.087

Then the sulphur and phosphorous content of this iron was increased by treatment with the following slag material:

Ferrous phosphate	26.0 gr.
Ferrous sulphide	28.0
Calcium fluoride	5.0
Aluminum oxide	3.0
Calcium carbonate	5.0
Silicon dioxide	22.0

Quantity of cast iron treated 1300 gr.

The iron was melted with this slag material, poured into a

mold, and allowed to cool. After cooling the sample was marked No. 4A and drillings were obtained and analyzed.

Results of analysis:

Carbon	2.81 %
Phosphorous	0.533
Sulphur	0.498

This sample, No. 4A, then received the following treatment. 1150 gr. of this iron was placed in a graphite crucible and the following slag material was added, with the object of lowering the sulphur and phosphorous content.

Calcium fluoride	5.0 gr.
Aluminum oxide	3.0
Calcium carbonate	10.0
Silicon dioxide	22.0

The crucible was then placed in the pot furnace and the contents heated to a molten condition. Then a covered iron crucible containing 35.0 grams of finely ground calcium carbide was dropped into the molten metal and the heating at a temperature of about 1500 degrees C. continued. Thirty minutes later another closed iron crucible containing 15.0 grams of calcium carbide was added, and this addition was immediately followed by the addition of twenty grams of calcium carbonate which was also contained in a closed iron crucible.

Thirty minutes later fifteen grams more of calcium carbide was added and followed by the addition of fifteen grams of calcium carbonate. Heating at a temperature of 1500 degrees C. was continued for twenty minutes, and the crucible was then removed

from the furnace and the molten metal poured into a sand mold and allowed to cool slowly.

This sample was marked No. 4B and an analysis made giving the following results:

Carbon	3.30 %	
Phosphorous	0.434	
Sulphur	0.272	
	Before Treatment	After Treatment
Carbon	2.81%	3.30 %
Phosphorous	0.535	0.434
Sulphur	0.408	0.272
Percent Sulphur Removed		33.3 %
Percent Phosphorous Removed		18.57%

Conclusions: This test gave a fairly efficient removal of sulphur and phosphorous and removal appears to be more complete by use of this method than by any of the previous methods tried.

The difficulty of maintaining the fluidity of a slag so rich in lime is one objection to this type of procedure.

TEST NO. 5

The object of this test was to determine the possibilities of sulphur and phosphorous removal by first treating the cast iron with calcium carbide in the pot furnace, and then removing it from the furnace and pouring it over a surface covered with calcium carbide.

Sample No 4B obtained by Test No. 4 was treated during this test. The composition in regard to carbon, phosphorous and sulphur was as follows:

Carbon	3.30 %
Phosphorous	0.434
Sulphur	0.272

This sample, No. 4B, was placed in a graphite crucible and the following slag material added:

Calcium Fluoride	10.0 gr.
Aluminum Oxide	6.0 gr.
Calcium Carbonate	20.0 gr.
Silicon dioxide	30.0 gr.
Calcium carbide	20.0 gr.

1670 grams of this iron was placed in a crucible and covered with the slag material. The crucible was placed in the pot furnace and heated at a temperature of about 1400 degrees C. for one hour. Then the crucible was removed from the furnace and the contents poured over a surface of calcium carbide, an illustration of which is shown in Fig. 1.

The molten metal solidified on this surface and due to rapid cooling was brittle enough to be broken into pieces. These pieces

were placed in a crucible and heated to a molten state and then poured into a sand mold.

After cooling the resulting sample was marked 5B, and analyzed giving the following results:

	Carbon	3.34 %	
	Phosphorous	0.325	
	Sulphur	0.120	
	Before Treatment		After Treatment
Carbon	3.30 %		3.34 %
Phosphorous	0.434		0.325
Sulphur	0.272		0.120
Per cent Sulphur Removed			55.88%
Per cent Phosphorous Removed			25.11%

Conclusions: This method of treatment gives the highest removal of sulphur and phosphorous and seems more efficient than any of the other methods studied, and it appears that the sulphur and phosphorous content of the metal can be reduced by allowing the metal to run over calcium carbide as it is pouring from the furnace.

RESULTS OF ANALYSIS

Test No. 1

Sample No.	1	1A	1B
Carbon	0.38 %	0.57 %	3.19 %
Phosphorous	0.082	0.711	0.402
Sulphur	0.038	1.304	1.10

Test No. 3

Sample No.	3	3A	3B
Carbon	2.866%	2.866%	1.765%
Phosphorous	0.552	0.552	0.307
Sulphur	0.136	0.136	0.129

Test No. 4

Sample No.	4	4A	4B
Carbon	3.45 %	2.81 %	3.30 %
Phosphorous	0.440	0.533	0.434
Sulphur	0.87	0.408	0.272

Test No. 5

Sample No.	5	5A	5B
Carbon	3.30 %	3.30 %	3.34 %
Phosphorous	0.434	0.434	0.325
Sulphur	0.272	0.272	0.120

SUMMARY OF RESULTS

	Original Sulphur and Phosphorous Content	Reduction in Sulphur And Phosphorous Content
Test No. 1	Sulphur 1.304% Phosphorous 0.711%	15.69 % 43.60 %
Test No. 2	Discarded	Discarded
Test No. 3	Sulphur 0.136% Phosphorous 0.552%	5.14 % 44.38 %
Test No. 4	Sulphur 0.408% Phosphorous 0.533%	33.3 % 18.57 %
Test No. 5	Sulphur 0.272% Phosphorous 0.434%	55.88 % 25.11 %

Summary:

1. When sulphur removal is at a maximum then phosphorous removal is at a minimum, and vice versa, due to the fact that reducing conditions must be present during the desulphurizing period and oxidizing conditions must prevail during the dephosphorizing period.

2. After dephosphorization with a slag rich in lime and metallic oxides, this slag, having a high content of $3\text{CaO} \cdot \text{P}_2\text{O}_5$, should be removed and a slag rich in lime and calcium carbide introduced into the furnace during the desulphurizing period.

3. During the dephosphorizing period comparatively low temperatures (1500 degrees C.) can be maintained, but during the desulphurizing period very high temperatures (2000 degrees to 2500 degrees C.) must exist so that the desired fluidity of the rich lime slag will be possible and the calcium carbide will not decompose.

4. Electric furnaces are the only type of furnace capable of producing temperatures high enough to accomplish complete refining of iron and steel, but because of the cost of operation are somewhat prohibitive.

5. The use of an electric furnace in conjunction with a Basic Open Hearth furnace or Bessemer Converter appears to be the ideal type of process for producing high grade steel.

Conclusions:

The fact that calcium carbide will exist only at very high temperatures makes its use in the Basic Open Hearth furnace impossible, and the application of calcium carbide to processes other than electric furnace processes seems to be a process of desulphurization and dephosphorization by allowing the molten metal to run over calcium carbide as it leaves the furnace, as described in Test No. 5.

Complete desulphurizing and dephosphorizing is not possible by this method but a considerable reduction of the content of these elements is effected by this method.

The danger of increasing the carbon content excessively in the case of low carbon steels is present, however, high carbon steel and cast iron could be treated in this manner.

Suggestions for Further Work:

1- The necessity of a furnace capable of producing temperatures of at least 2000 degrees C cannot be too greatly emphasized in work of this character.

2- With these high temperatures the importance of crucibles made of refractory material capable of withstanding this heat also presents itself.

3- A study of the rate of desulphurization and dephosphorization with variations in time would furnish important data.

BIBLIOGRAPHY

B. Stoughton- - - "The Metallurgy of Iron and Steel."

1903, Published by McGraw-Hill Book Co.

New York, New York.

This book gives a good description of the manufacture and mechanical treatment of steel and cast iron. It also contains much information upon the heat treatment of steel, and a discussion of alloy steels.

Hall and Williams "The Chemical and Metallographic Examination of Iron, Steel and Brass".

1921, Published by McGraw-Hill Book Co.

New York, N. Y.

It is from this book that the methods of analysis used in this thesis work were taken, and this book gave the most complete and simple analysis method for every element in steel. There are several micro-photographs shown along with a complete discussion of metallographic methods.

K. Dichmann- - - "The Basic Open Hearth Process"

1911, Published by D. VanNostrand & Co.

New York, N. Y.

This book, written by a technical man gives a good description of the Basic Open Hearth Process and conditions required for maximum removal of sulphur and phosphorous.

Camp and Francis "The Making, Shaping and Treating of Steel."

1920, Published by the Carnegie Steel Co.

Pittsburg, Pa.

The complete description of the manufacture of all types of steel as presented in this book makes this book indispensable to anyone interested in iron and steel.

C. H. Fulton - "Principles of Metallurgy."

1910, Published by the McGraw-Hill Co.

New York, N. Y.

This is a very good book to get the basic principles from on the solution theory of carbon and iron, as well as some information on metallurgical operations in general. The information obtained from this book combined with a further discussion as given in B. Stoughton's "Metallurgy of Iron and Steel," should make the solution theory very simple.

A. Sauveur- - "The Metallography and Heat Treatment of Iron and Steel."

1916, Published by Sauveur and Boylston.

Cambridge, Mass.

This book gives a complete discussion of steel in regard to its various elements, heat treatments, and Metallographic Methods, along with numerous microphotographs.

Rodenhauser, Schoenawa and Vom Baur "Electric Furnaces in the Iron and Steel industry."

1917, Published by J. Wiley and Sons, London, Eng.

A complete description of the manufacture of steel in electric furnaces is given in this book with special reference to the slag material and reactions.

PERIODICALS

Journal of the Iron and Steel Institute

This journal contains many interesting articles pertaining to iron and steel among which the following was most interesting and appropriate to this thesis.

J. O. Arnold and G. B. Waterhouse- - "The Influence of Sulphur and Manganese on Steel."

No. 1 1903. pp 136-160

Journal of Ind. and Engineering Chemistry

This journal although dealing chiefly with chemical reports often contains articles on metallurgy. The article on an absorption tower for CO₂ was especially applicable to this work.

"Sodium Hydroxide as an Absorbent for Carbon Dioxide."

Kelly and Evers, Nov. 1921 page 1052

Chemical and Metallurgical Engineering.

Several articles pertaining to this work were found in this journal among which the following were most important:

"Deoxidation and Desulphurization in the Heroult Furnace".

F. T. Sisco Jan. 4, 1922 pp 17-22

"Desulphurizing Cast Iron"

May 10, 1922 p 887

Chemical Abstracts.

A summary of each of the various articles presented to the

chemistry field is given in this publication of the American Chemical Society.

The abstract of an article entitled, "The Desulphurization and Dephosphorization of Iron and Steel by Slags,"

14, 2151-52 1920, was of special interest.

Journal of the American Chemical Society.

Several articles of metallurgical interest, although not pertaining directly to this work were found in this periodical.

The following periodicals were also consulted:

The Iron Age

The Foundry

The Iron Trade Review.

UNIVERSITY OF ILLINOIS-URBANA



3 0112 101353271